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Three-Layer PdO/$CuWO_4$/CuO System for Hydrogen Gas Sensing with Reduced Humidity Interference

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Abstract: The growing hydrogen industry is stimulating an ongoing search for new materials not only for hydrogen production or storage but also for hydrogen sensing. These materials have to be sensitive to hydrogen, but additionally, their synthesis should be compatible with the microcircuit industry to enable seamless integration into various devices. In addition, the interference of air humidity remains an issue for hydrogen sensing materials. We approach these challenges using conventional reactive sputter deposition. Using three consequential processes, we synthesized multilayer structures. A basic two-layer system composed of a base layer of cupric oxide (CuO) overlayered with a nanostructured copper tungstate ($CuWO_4$) exhibits higher sensitivity than individual materials. This is explained by the formation of microscopic heterojunctions. The addition of a third layer of palladium oxide (PdO) in forms of thin film and particles resulted in a reduction in humidity interference. As a result, a sensing three-layer system working at 150 °C with an equalized response in dry/humid air was developed.

Keywords: conductometric hydrogen sensor; copper tungstate; $CuWO_4$; reactive sputtering; nanoheterojunction

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1. Introduction

As a prominent clean source of energy, hydrogen plays an important role in power generation. Its vast abundance, non-toxic nature, and high combustion efficiency make it a promising source of energy in the future. The highly flammable, bland, odorless, and colorless character and wide explosive concentration of hydrogen demand the development of sensors and detectors. Among many approaches, one of the most common are chemiresistors based on metal oxide semiconductors (MOS) [1–4].

Primarily, binary oxides such as WO_3, TiO_2, SnO_2, CuO, NiO, etc., have been investigated as chemiresistors. Along with the demands for better performance, novel approaches have been employed such as the formation of heterojunctions by combining more than one MOS [5–7], the addition of catalytic metal particles onto MOS (Pt, Pd, Rh, etc.) [8–11], MOS nanostructuring [12–15], and MOS doping or the formation of ternary MOS [16,17]. Ternary oxides such as Zn_2SnO_4 [18], $ZnWO_4$ [16,19], $NiWO_4$ [20], and $CuWO_4$ [21,22] are attractive candidates for the research in this field. Copper tungstate ($CuWO_4$) is a promising chemiresistor due its chemical and thermal stability and the presence of metal cations Cu^{2+} and W^{6+} providing adsorption sites [23–25]. Only a few research works have been performed on the combination of $CuWO_4$ with other materials. For example, $CuWO_4$/CuO heterojunctions were prepared using wet-based techniques [26–28]. However, these techniques limit the control of the purity and the composition of the final material. In our recent work [22], we investigated the combination of $CuWO_4/WO_{3-x}$ layers prepared by reactive sputtering, which is a deposition technique compatible with the thin-film industry and does not require a high temperature for synthesis.

With the design and development of novel MOS sensing materials, well-known cross-sensitivity to air humidity remains a crucial factor that needs to be addressed. Several

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